The Effect of Incorporation of HNO_3 into Liquid Sulfuric Acid on Heterogeneous Reaction Probabilities

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Using a fast-flow reactor coupled to a quadrupole mass spectrometer, the heterogeneous reactions of $ClONO_2$ + HCl and HOCl + HCl as well as hydrolysis of N_2O_5 and $ClONO_2$ were investigated on liquid sulfuric acid, with particular emphasis on the effect of incorporation of HNO_3 on the reaction probabilities. The detection scheme utilized both electron impact (EIMS) and chemical ionization (CIMS) mass spectrometry. By maintaining a constant water partial pressure typical of the lower stratosphere, we were able to simulate the composition representative of the stratospheric sulfate aerosols. Reactive uptake coefficients of $ClONO_2$, HCl, and HOCl were studied on the $H_2SO_4/HNO_3/H_2O$ ternary system, which has recently been proposed to form at conditions pertinent to high latitudes in the winter and early spring. These heterogeneous reactions could promote chlorine activation on the sulfate aerosols, even in the absence of polar stratospheric clouds. Also, the hydrolysis of N_2O_5 and $ClONO_2$ on stratospheric sulfate aerosols may not be known precisely because previous laboratory measurements were not conducted at the exact stratospheric conditions; these reactions are important to repartitioning the stratospheric NO, concentration in mid-latitudes. Reaction probabilities for N_2O_5 and $ClONO_2$ hydrolysis were measured in the presence of gaseous HNO_3 at stratospheric concentrations in order to mimic the process occurring in the stratosphere. Stratospheric implications of the present measurements will be discussed.

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